When the eye is looking nearly in the right direction, the spectrum appears to be covered by a veil proceeding from the red end up to a point dependent upon the precise direction of the light. By slightly shifting the eye, the veil may be made to reach any desired part of the spectrum, and then we know for what ray total reflection is just commencing. By bringing the veil to touch the soda line (rendered visible with the aid of the spirit lamp), precisely the same direction was found as had previously been marked out with use of homogeneous light. It would be possible in this way to determine with considerable accuracy the dispersive powers of opaque bodies.

The angle of 18°, being measured in air, is not the complement of the true angle of reflection. If we take 1·630 as the index of CS_2 for soda light, we find for this angle

$$\sin^{-1}\left(\frac{\sin 18°}{1·630}\right)=10° \; 56' \; ;$$

whence for the index of the glass relative to soda light,

$$\mu = 1·630 \cos 10° \; 56' = 1·600.$$

The amount of reflection according to Fresnel's formula, with an incidence of 13° 52' and an index 1·600, is 0·05726, a little *less* than that actually observed. The agreement is as good as could be expected, but it should be noticed that this mirror was merely cleaned and not repolished with putty powder. If repolishing were to produce as much effect in this case as upon the acute-angled prism (I), Fresnel's formula would be left considerably in arrear.*

P.S. Nov. 9, 1886.—I am indebted to Mr. Glazebrook for a determination of the refractive index of the prism of crown glass II. He finds $\mu = 1·5328$. The introduction of this into Fresnel's formula ($\theta = 13° \; 52'$) gives for the reflecting power 0·0477.

V. "A Theory of Voltaic Action." By J. BROWN. Communicated by Lord RAYLEIGH, Sec. R.S. Received October 4, 1886.

[PLATES 4 AND 5.]

1. From a series of experiments made more or less continuously during the last five years the following conclusions have been drawn:—

That the difference of potential near two metals in contact as observed either by the bi-metallic condenser (Volta's) method,

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* Some of the results here given were communicated to the British Association at Birmingham, where also was read a paper by Sir John Conroy on the same subject.

or by the bi-metallic ring or quadrants method of Sir William Thomson, is due to the chemical action of a film of condensed vapour or gas on the surfaces of the metals.*

That the two metals with their liquid or quasi-liquid films are quite similar to a galvanic cell composed of the same metals as elements, and a liquid similar to that of the films as electrolyte ; the said electrolyte being (in the ordinary static "contact" experiment) divided by the intervening insulating diaphragm of air or other gas.

2. Therefore in these experiments it is the difference of potential at the outer surfaces of the two films that is measured.

In the case of a single metal, *e.g.*, zinc covered by its chemically active electrolytic film, there is, according to the view here advocated, at the surface of contact between the film and the metal, an electromotive force due to the chemical action between them, charging the zinc negatively and the film positively. The two charges being bound have no outer manifestation of any kind.

Copper again, for example, is affected similarly, but less strongly, than zinc. If it be connected metallically to the zinc, the potentials of the metals will be equalised, a portion of the negative charge going through the connexion from the zinc to the copper and thence to the film on the copper.

3. This theory as applied to the Volta condenser experiment is referred to somewhat in detail by Wiedemann ('Die Lehre von der Elektricität,' vol. 2, pp. 986—987) ; and the view held by De la Rive ('Traité de l'Électricité,' vol. 2, 1856, p. 776) was very similar, differing mainly in the supposition that the positive charge separated off in the film was maintained there by the insulating nature of the film, whereas it is evident that an electromotive force at the surface of contact of the film with the metal sufficient to cause the separation of the two charges will also be sufficient to keep them separate. We are, therefore, in so far not debarred from considering the film an electrolytic conductor. De la Rive's view seems, however, to have received little general attention, perhaps less than it deserved.

4. It seems advisable to discuss these views experimentally while trenching as little as possible on the uncertain domain of speculative molecular physics, and in describing the experiments I shall refer in detail to those only which gave reliable results. Many preliminary trials were made before disturbing causes were eliminated, and many negative results were obtained. It has, however, been gratifying to find that no reason has appeared requiring the alteration of anything in the two short papers previously published on this subject ('Phil. Mag.,' Aug., 1878, Feb., 1879).

* [No account is here taken of any infinitesimal effects that may be due to thermo-electric action, &c.—December 3, 1886.]

5. The principal piece of apparatus used was a bi-metallic quadrant electrometer represented at fig. 1, about one-fourth actual size. Its design was an elaboration of the temporary apparatus described in a previous paper (' Phil. Mag.,' vol. 2, 1878, p. 142). A is a metal case supported on levelling screws ; B a thick vulcanite tube provided at its upper end with a brass cap containing a collar of leather in which slides the brass rod C. D is a brass ball with clamping screw to retain the rod at any desired height. E is a platinum torsion wire, 0·001 inch diameter, carrying the stouter wire F, on which are fixed a light concave mirror G, the " needle " H, and a glass weight J dipping in water or other liquid contained in a glass vessel, resting on a vulcanite plate on the bottom of the instrument. R and L are the quadrants of the metals under examination screwed to a vulcanite piece M which is adjusted by hole, slot, and plane on the points of three long fine-threaded levelling screws, O, P, Q, passing up through stuffing-boxes in the bottom of the instrument. The quadrant L is connected to an insulated wire N passing out air-tight through the back of the case. R is connected to the body of the instrument and to " earth " by a slip of foil under the vulcanite support touching the screw O. A stopcock T in the top of the vulcanite tube and another in the bottom of the instrument of which the opening is shown at S, provided means for varying the nature of the gas surrounding the metals. The opening in front of the instru-ment was provided with a flange, faced up to a plane, on which a pane of plate glass was jointed by grease or other suitable means. The needle was electrified either positively or negatively by connecting its suspending wire through a Pohl's reversing commutator to either pole of a battery of 100 small Daniell cells : the opposite pole being at the same time connected to the body of the electrometer and to " earth."

6. To make an experiment with this apparatus the quadrants were first carefully adjusted with their upper surfaces in the same plane, then put in position, roughly levelled, the connexion to wire N made, and the pair dusted with a camel-hair brush. The needle which had been raised by the sliding-rod C was now lowered to within about 0·05 inch of the surface of the quadrants, and adjusted with its centre line over the slit between them and its suspension wire in the centre of the system.

If now on connecting the quadrants metallically, and electrifying the needle positively and then negatively, it was found that the deflection (as observed by lamp and scale) was greater on one side of zero than on the other, due to one quadrant being higher than the other, the necessary adjustment was made by means of the screws O and P. A second concave mirror fixed on the ball D was now clamped, so that its reflected beam also fell on the zero of the scale,

so that after raising the rod C it could be readily brought back to its original position. The quadrants were now levelled by a spirit-level from front to back, after which the difference of potential might be at once taken, or they might be removed again to be cleaned, rapidly replaced, and a reading taken as quickly as possible afterwards without the loss of time in adjusting them. A "reading" was taken by causing the needle (by reversing its potential twice) to deflect first on one side (say right) of zero, then to the left, and again to the right. The mean of the two right-hand deflections was added to the left-hand one in order to eliminate the effect of a slow shifting of the zero which sometimes occurred, caused apparently by a slow untwisting of the suspension wire, or a slight warping of the vulcanite piece M.

7. The readings were either qualitative when the two quadrants were put in metallic connexion, or quantitative when the difference of potential of their films was compared with a standard cell.

In order to make the connexions conveniently for both kinds of readings a modified Pohl's commutator was used, by means of which the quadrants could either be directly connected with each other, or else one to each pole of the standard cell W in either sense.

8. At first two standard cells were used, a Clark's cell purchased from Elliot Brothers, and a Daniell constructed as at W. X, Y, Z are three test-tubes fixed in a block of paraffin. X contains a half-saturated solution of zinc sulphate, with a rod of redistilled zinc not amalgamated. In Z is a gutta-percha covered copper wire, having its lower end cleaned, wound into a spiral, and covered with crystals of copper sulphate and water. Y contains distilled water with a strip of zinc to reduce any copper salt that might diffuse over from Z.

When the Clark's cell was used, the results were reduced to the Daniell as unit value. Comparisons with both cells were at first frequently made.

9. The measurement of the difference of potential near any pair of quadrants was made by a well-known method as follows. The cell was first connected, so that its electromotive force should increase the deflection due to the difference of potential near the quadrants, and a reading a taken. The connexion was then reversed, and a reading b taken. If d is the deflection due to the standard cell, and p that due to the difference of potential near the quadrants—

$$d+p=a$$
$$d-p=b$$
$$\text{therefore} \quad \frac{p}{d} = \frac{a-b}{a+b}.$$

For example, in comparing the difference of potential of the films on slightly tarnished copper and zinc in air the following deflections were found—

Copper of cell to zinc quadrant—
  Right, 76 ; left, 75 ; right, 74·5. $a = 150·25.$
Copper of cell to copper quadrant—
  Right 19·5 ; left, 11·5 ; right, 20·5. $b = 31·5.$
     Whence $p = 0·65$ Daniell.

Owing to the nature of the apparatus, extreme accuracy in the results as absolute quantitative measurements is not to be expected. They are meant in most cases more for comparisons among themselves.

10. A number of experiments were made to ascertain the rate of decrease of difference of potential of the films on copper and zinc in air due to gradual tarnishing of the metals. The curves corresponding to two of these with zinc of different degrees of purity are given in fig. 2, where ordinates are in decimals of the electromotive force of one Daniell, and abscissæ represent the time elapsed after cleaning the metals with glass paper. Ten more observations were made on the pair of copper and redistilled zinc giving curve A. The remainder of the curve has the same character, falling in 61½ hours to 0·64 Daniell.

The object was to estimate the difference of potential due to the clean metals by carrying the curve back to the time at which they were cleaned, and compare this with the difference of their heats of combustion in oxygen as compared with the heat equivalent of the standard cell. The result agrees fairly well with the thermochemical data of J. Thomsen ('Wiedemann, Beiblätter,' 1880, Nos. 7 and 8).

We are met, however, with the fact that with many other pairs of metals in air we do not find the same agreement, although in most cases there is a more or less near approximation. This I believe is due to two causes :—

(1.) We cannot tell the exact nature of the chemical process going on at the surface of the metals, whether it be simply an oxidation ; which particular oxide of the metal is formed, or if the other gases, ammonia, carbonic acid, &c., take any part in the process, nor do we know exactly the physical state of the film.

(2.) We do not know how much protective effect the already formed coating of oxide, &c., exercises on the metals.

11. The comparatively small and often irregular difference of potential observed when experimenting with copper and iron may be due to the formation on the latter, immediately after cleaning, of a highly protective oxide coating, producing a more or less passive state analogous to that which this metal assumes under other well-known conditions. The rapid tarnishing of lead may also produce a similar effect supposing the oxide formed be of a very coherent and protective nature.

The consideration as to which oxide is formed leads to the question whether any difference of potential would be found near the contact of two different oxides of the same metal—I experimented on litharge and red lead, and on stannous and stannic oxides, but did not get results sufficiently definite to be reliable—but I think the experiments worth repeating with freshly-formed oxides, which mine were not.

12. It has been suggested in criticising my former experiments on the effect of various gases on the difference of potential near certain metals in contact, that it would have been better to have had quantitative results. Although for the reasons given above these are perhaps not of very much value, I have, however, made measurements in several cases. The following are the results with a copper-iron pair in hydrogen sulphide gas.

Quadrants of these metals after being freshly cleaned with glass-paper were put in position, and the difference of potential in air measured as quickly as possible was found to be 0·059 D, 0·062 D, mean 0·06 D, iron side positive.

Hydrogen sulphide was now sent into the electrometer, reversing immediately the relative potentials near the metals. The stopcocks were then closed and the following measurements taken:—t representing the time elapsed after admission of the gas, and P/D the ratio of the difference of potential near the metals to that of the terminals of a Daniell cell.

t.	8 m.	15 m.	25 m.	1 h. 18 m.	2 h. 10 m.	2 h. 35 m.	12 h. 10 m.
P/D.	0·4	0·48	0·53	0·55	0·47	0·43	0·3

Some fresh hydrogen sulphide now sent in caused a slight rise, P/D = 0·32, after which it fell slowly, and in about 11 hours more ($t = 23$ h. 25 m.) it was 0·26. The instrument was now cleared of gas and left open for about $1\frac{1}{2}$ hours, when P/D fell to 0·1. Re-admission of gas raised it to 0·32. This was repeated with the same result, after which the instrument was left open for 24 hours, when the iron side was found positive, P/D = 0·32. This somewhat high value may be due to oxidation of the iron sulphide, but more probably perhaps to oxidation of the iron itself, coupled with the protective action of the very thick coating of sulphide on the copper. After again admitting the gas the copper side became again positive, P/D = 0 26 D. Several more changes of the atmosphere were made, the corresponding change in difference of potential taking place each time. The electrometer was then charged with the gas and closed up, the water vessel having been removed (so that its vapour might not interfere with insulation inside the instrument), and its place supplied by paper vanes cemented to the weight. The difference of potential then fell gradually till at the end of eight days after the gas had first acted on the metals it was sensibly zero. On opening the electrometer plenty

of the hydrogen sulphide was found still present in it, and the metals
were much corroded; the copper brown with lighter patches; the
iron greyish with patches also, but having a thinner coating of sul-
ph de than the copper.   On allowing the metals to remain exposed to
the air, the iron side became again gradually more positive; the
difference of potential rising during 26 hours to 0·26D, after which
it fell in about a week to 0·22D.

13. As the electrochemical relation of silver and iron in water is
also reversed when solution of potassium sulphide is added, I had
little doubt that an addition of hydrogen sulphide to the air about
these metals when in contact would reverse the potentials near them.

To test this the upper surface of the copper quadrant used in the
last experiment was covered with a piece of thin silver sheet cemented
on, thus forming a silver-iron pair with the iron quadrant.   The
difference of potential just after cleaning the metals with emery- and
glass-paper was 0·23D, iron side positive.   In three minutes after
admission of the gas the next reading showed the silver side positive;
difference about 0·4D.   The following readings were then taken,
t as before the time after admission of the gas.

t.	12 m.	16 m.	1 h. 0 m.	23 h. 40 m.	33 h. 30 m.	58 h. 40 m.
P/D.	0·42	0·44	0·43	0·38	0·35	0·35
			84 h. 20 m.	94 h.		
			0·365	0·38		

The sulphide formed on the inside of the metal case of the instru-
ment by the action of the gas, now began to peel off in scales and
jammed the vanes of the weight.   After cleaning these out fresh gas
was sent in, and P/D became 0·36D; silver side still positive.
Measurements were then made at intervals, the difference of potential
falling gradually to 0·23D, on the fourteenth day after admission of
the gas at the outset.

By that time, however, the gas was found to have been all or
nearly all absorbed by combination with the metals and the sides of
the instrument.   The conclusion of the experiment is therefore in-
complete, but it indicates that the difference of potential decreases
with these metals also, although more slowly than with copper and
iron.

14. It was suggested by Mr. Cross, of Barrow-in-Furness, that the
difference of potential near a copper-iron pair in air and in ammonia
gas should be compared.   The electromotive force of a cell formed by
these metals immersed in distilled water is about 0·35D, copper the
positive pole, but if ammonia solution be added, this electromotive
force reverses and becomes 0·27D.

Three experiments were made with copper-iron quadrants in this
gas, which was sent into the instrument by boiling strong liquor

ammoniæ in a flask connected by glass tubing to the stopcock T. In each case the potential was reversed, and the difference of potential appeared rather less in the ammonia atmosphere than in air, but owing to the action of the gas on the vulcanite piece M, causing it to twist and so alter the position of the quadrants, I was unable to get reliable quantitative comparisons with the standard cell.

15. In a cell composed of copper and nickel in distilled water, nickel is the positive metal, and the electromotive force is about 0·24D. On adding a few drops of a solution of ammonia a reversal takes place and copper becomes the positive metal. The electro-motive force appears at first rather greater than that of the water cell but falls off quickly.

The analogous experiment with gaseous ammonia was made in a qualitative way only. The quadrants of the electrometer were re-placed by a flat ring half copper and half nickel, the two metals soldered together. (This had been used in a former experiment with hydrochloric acid gas.)

The metals of the ring having been rubbed bright with emery-paper, the potential in air only near the nickel was positive to that near the copper, the index passing over about $4\frac{1}{2}$ divisions, when the electrification of the needle was reversed.

After admitting ammonia gas in the same way as before described the copper side became positive, at first slightly, but after two hours the index moved over six divisions for a reversal of the needle. The two kinds of experiments therefore agree here also fairly well.

16. I now sum up the results (regarded qualitatively only) ob-tained in this kind of experiment, where a change in the constituents of the atmosphere surrounding a pair of metals in contact reverses the difference of potential near them in correspondence with the reversal of electromotive force, which takes place after a similar change in the corresponding liquid electrolyte used with the same metals as a voltaic cell.

Pairs of metals.	Compound whose addition in solution causes a reversal of electromotive force in a hydro-element or cell.	Compound whose addition as gas to the atmosphere surrounding the metals in contact causes a reversal of the difference of potential observed near them.
Copper-Iron	Potassium sulphide	Hydrogen sulphide.
Copper-Iron.....	Ammonia	Ammonia.
Silver-Iron	Potassium sulphide.......	Hydrogen sulphide.
Copper-Nickel ...	Ammonia...............	Ammonia.
Copper-Nickel ...	Hydrochloric acid........	Hydrochloric acid.

These are the only cases tried ; no exception has, therefore, been found by me, nor, so far as I know, by others.

17. One of the most ingenious explanations (from the pure contact theory point of view) of the change of potentials near the copper-iron or copper-nickel pair effected by hydrogen sulphide or chloride is that of G. Wiedemann ('Lehre von der Electrikität,' vol. 1, p. 205), who suggests that in addition to the films of sulphide or chloride formed on the metals, a film of hydrogen may be deposited, and the contact effect of all these substances is added to that of the metals. It may be pointed out that precisely the same explanation may be given of the usual experiments made in presence of water-vapour where the oxygen combining with the metal forms an oxide film, which may again be covered with the hydrogen left free.

18. Several other authors have urged as an objection to these experiments, that the action of the gases causes the formation of coatings of various compounds, and so the whole state of things is altered by the introduction of additional bodies or substances assumed to introduce new so-called " contact effects." (See Ayrton and Perry, ' Phil. Mag.,' January, 1881, p. 48 ; Pellat, ' Journal de Physique,' vol. 10, 1881, or ' Thèses présentées à la Faculté des Sciences de Paris,' No. 461, p. 16.)

Dr. Lodge also states ('Brit. Assoc. Report,' 1884, p. 50), " but satisfactory observation in these gases is difficult, because they not only *tend* to attack the plates, but they *do* attack them, and so a film is formed and everything is rendered uncertain."

But it is surely too much to say that no such film (of oxide) is formed in the experiments as usually made in air. We are even justified in inferring that such a thing as a " contact" experiment on clean metals has not yet been made, since they are invariably cleaned while exposed to the atmosphere, and therefore covered with a layer or film of highly condensed water-vapour containing other dissolved gases.

Each abrading point of the polishing material (emery, glass-paper, or whatever it be) may almost be said to be working under water on the metal.

It seems difficult to suppose that even for an instant after each little abrading point has passed, the surface of the metal exposed in its track remains unoxidised. All such critics assume quite unwarrantably that in the old contact experiments of Volta the surface of the plates is not altered by the atmosphere, whereas the alteration is not only after a time visible to the naked eye, but is accompanied by a sequence of electrical effects in a quite similar way to that when other gases are used, which attack chemically one or other of the metals, so as to mask or overpower the action of the oxidising atmosphere still present. On the other hand, when gases are added

that have not an action differing from that of the air (still present to a greater or less degree), or are merely neutral, there is no great difference in the electrical effects produced (Pellat, ' Thèses présentées à la Faculté des Sciences de Paris,' p. 109 ; Schulze-Berge, 'Wiedemann, Annalen,' vol. 12, 1881, p. 293). The effect of a hydrogen atmosphere in gradually decreasing the negative potential near platinum is an exception, and has been already well explained by the hypothesis that it forms an alloy with the platinum of a more positive character ; or which, according to the chemical theory, has a greater affinity for the oxygen still present than the platinum has.

19. Many attempts have been made to remove completely from the metals under examination all oxidising or other chemically active substances, and thus show that the metals *per se* have no power of producing a difference of potential.

Some of the older writers claim to have effected this by thickly varnishing the plates of the copper-zinc Volta condenser. I doubt if even a thick coat of varnish, which is more or less pervious to gaseous matter, would so effectually protect the surfaces as to leave no effect discernible by the more sensitive modern appliances. Besides, the varnish itself is objected to as a new element in the chain of " contact" effects. Some experiments on the effect of varnish were made with the large Volta condenser shown at fig. 3.

20. This instrument was in general form copied from that described by Schulze-Berge (' Wiedemann, Annalen,' vol. 12, 1881, p. 294). Referring to fig. 3, A is a triangular piece of mahogany 1 inch thick, turning on pointed screws at B, and resting at its other end on a support M. It carries on its lower surface three vulcanite fittings, DD, supporting the copper plate C, which can thus be raised from or lowered towards the zinc plate Z, lying on three vulcanite levelling screws, SS. The plates were 8 inches diameter, and about $\frac{1}{4}$ inch thick.

A measurement of the difference of potential of the films on these plates was made by a method similar to that employed by Schulze-Berge and shown at fig. 4, where D is a Daniell's cell, of small internal resistance, connected to RR', a set of resistance coils, of which the part a is 200 ohms and x is variable. The key K breaks the connexion of both the condenser plates Cu, Zn at once. In making an experiment the resistance x was adjusted till on breaking the contacts at K, and immediately afterwards separating the plates, no sensible deflection was observed at the quadrant electrometer E in connexion with them. Then the amount of resistance in x divided by the whole resistance RR' gave in terms of the Daniell the difference of potential required to neutralise that of the films.

21. The zinc plate of this condenser was carefully varnished all over while hot with repeated coats of " silver lacquer " (shell-lac and other gums dissolved in spirits of wine), but the difference of

potential between the varnish on the zinc and the film on the opposed copper plate did not fall below 0·29D taken while the zinc was hot.

On cooling for 15 minutes the value rose to 0·35D, and after some hours to 0·46D, an effect easily caused by the passage of moisture into the varnish.   Fifteen hours after it had fallen to 0·4D, indicating probably the formation of a partially protective coat of oxide under the varnish.

The commonly accepted value for plates of these metals recently cleaned in air is about 0·8D.

22. I have also endeavoured to obtain this result, although without much hope of success, by immersing the platinum-zinc quadrants of the electrometer, fig. 1, in naphtha which had been digested with metallic sodium for several months in order to free it if possible from oxidising matters.   Metallic sodium was also placed on the bottom of the electrometer.   The naphtha was contained in a glass jar, and connected by a syphon to the stopcock S.   The difference of potential of the polished metals measured in air was 0·88 D.   The naphtha was now run in for five minutes, when its level was about 0·05 inch over the surface of the quadrants, and about the same distance below the needle.   The following observations were then made ; t denoting time elapsed after the metals had become covered :—

$t=8$ m.	40 m.	1 h. 40 m.	2 h. 40 m.	4 h.	7 h.	12 h.	22 h.
0·66 D	0·61D	0·49D	0·5D	0·49D.	0·39D.	0·39D	0·31D.

Two hours after this last observation the naphtha was partially run out of the instrument, so as to bring its surface below the level of the quadrants, when a measurement gave only 0·23D.   It is difficult to see why the thin film of naphtha still present on the plates should possess a more protective power than the bulk of the liquid.

It may be that there was in the naphtha some small quantity of water or other substance chemically active towards the zinc (the deterioration of sodium or potassium under naphtha is well known) which would soon become exhausted from the thin film, but the hypothesis is open to doubt.

23. Faraday considered that electrolytic " decomposition and the transference of a current are so intimately connected that one cannot happen without the other " (' Exp. Res.,' vol. 1, p. 252).   I think it in the highest degree probable that the same theory applies to the production of the momentary current which gives rise to a difference of potential near the surfaces of two apparently dry metals when placed in contact, and that the electrolyte then active consists of the water supplied from the air and condensed in invisible films on them. Hence the chemical action producing the electrical effect is not only

the mere oxidation by free oxygen, but is associated with the decomposition of the condensed film on the metal.

24. The apparatus, fig. 1, was admittedly not sufficiently impervious to gaseous diffusion to permit of a crucial experiment on the effect of drying the atmosphere surrounding the metals. However, in the hope of partial success, the following experiment was begun in 1884. The copper and zinc quadrants were adjusted in position, the water vessel having been removed, and a weight with paper vanes substituted. The difference of potential was found 0·68D. Two small porcelain capsules containing phosphoric anhydride were placed inside the instrument, and the joint between the glass front and the metal facing made as good as possible with grease. The following measurements were then made in terms of standard Daniell; t in this case standing for days after closing up the instrument.

$t=0$	1	2	3	5	7	9	11	13
P/D=0·64	0·62	0·64	0·61	0·59	0·59	0·58	0·58	0·57

$t=20$	35	78	124	134	304	305
P/D= 0·56	0·56	0·557	0·54	0·50	0·52	0·51

The phosphoric anhydride was now taken out, and the instrument allowed to remain open for twenty minutes, after which a very carefully made and satisfactory observation showed that the difference of potential had increased to 0·646D. Fresh phosphoric anhydride was now placed in the instrument, which was closed as before, and the value measured immediately afterwards found to be 0·659D.

A similar series of observations was then made for a period of 173 days, during which the observed difference of potential fell more or less regularly to about 0·5D. Then on allowing the instrument to remain open for one hour it rose to about 0·67D. These results were quite as marked as I had hoped for with such unsuitable apparatus, and seem to show very clearly that even a partial drying of the metallic surfaces alters the difference of potential near them in a decided manner.

25. In 1881 I had endeavoured to construct a copper-zinc quadrant electrometer hermetically sealed in a glass vessel, from which I could exhaust the air and absorb the oxygen compounds by potassium. Repeated failures in the construction of the apparatus have hitherto debarred the experiment. A similar idea occurred to Herr Von Zahn about the same time ('Untersuchungen über Contact-Elektricität,' p. 48).

He enclosed a platinum-zinc condenser in a hermetically sealed tube, together with metallic sodium. The difference of potential was reduced in this case to about 0·5D, which the author attributes, in part at least, to the absence of moisture. He considers the experiment

would be a crucial one in favour of the chemical theory, if, after opening the tube, the difference of potential was found to have increased.   He does not, however, open it.

There are two objections to this particular experiment.   The tube, &c., was washed out with water which tarnished the zinc. The action of the sodium on moisture would evolve hydrogen, which would alloy with the platinum.

The former would reduce the difference of potential permanently, and the latter perhaps temporarily, but neither would, I think, much affect the conclusion to be drawn from a measurement made immediately on opening the tube.

26. Von Zahn also experimented qualitatively on the difference of potential between a copper plate and a flat spiral of glass tube containing sodium used as a Volta condenser plate, but does not seem to have tested the effect after the lapse of any considerable time, although he states that the surface of the sodium remained bright after standing some years.

If Bunsen's hypothesis ('Phil. Mag.,' vol. 17, 1884, p. 172) that glass may gradually, year after year, absorb a part of the liquid film in contact with it, be true, it would probably be necessary to allow such apparatus to stand a long time before the absorbed water had freed itself from the glass.   The same criticism applies to Von Zahn's experiment with a sodium copper condenser *in vacuo*, where the tube broke after the first observation.

27. The foregoing observations, the fact that gases under ordinary conditions are non-conductors, and the much greater simplicity of the theory, all point to the view that the so-called " contact " effects are due to the action of condensed films on the surface of the metals. When the copper and zinc quadrants are wet with water, the difference of potential near them is practically that of the terminals of a cell formed of the same metals dipping in water.   If instead of the water we use copper sulphate saturated solution on the copper quadrant and zinc sulphate solution on the zinc, the difference of potential is almost exactly that of the Daniell cell, of which this arrangement is the analogue.   In fact whether we break such simple galvanic circuits in their metallic parts, or in their liquid parts, we obtain the same value at the terminals in either case.

28. Considering then the two metals of a copper-zinc Volta condenser as the elements of a cell, and the moisture film on them as the electrolyte, we have a simple copper-water-zinc cell, divided on its electrolyte, and showing, when the metals are clean, approximately the difference of potential appropriate to such a cell.

The well-known experiment of Sir William Thomson, where a water-drop was placed between the previously disconnected metal quadrants, is thus easily explained.   The water-drop connexion

equalised (sensibly) the potentials of the films, by altering those of the metals which were previously at one potential.*

29. Evidently then, as I have before suggested ('Phil. Mag.,' Feb., 1879), in experiments purporting to give the difference of potential between a metal and a liquid by the condenser method, such as those of Hankel, Gerland, Clifton, Ayrton and Perry, &c., we have really a two-fluid cell (one fluid being that under examination and the other that condensed on the metal plate), with a dielectric division of air between the two fluids. Any observed differences of potential can readily arise from differences between the nature and constitution of the film and those of the liquid under examination, even if the latter be water. The film can, for instance, more easily replace by absorption from the air any oxygen in solution which may have entered into combination with nascent hydrogen liberated by the oxidation of the metal.

These differences naturally cause different actions on the metal, entailing different states of its surface, which again react on the electrolytes differently.

If in experiments of this kind the metal dipping in the liquid be different to that of which the plate is formed, we have of course then a two-metal two-fluid cell.

30. This aspect of the Volta condenser as a copper-fluid-zinc cell divided in its electrolyte, suggested the possibility of joining the films only on the two metals, without bringing the metals themselves in contact, and so producing a real galvanic current-producing cell from the apparently dry metals. This I succeeded in doing after a very great expenditure of time and patience; an expenditure partly owing to the unsuitability of the apparatus—the condenser, fig. 3, described § 20, having been designed for another purpose, was not capable easily of sufficiently fine adjustment. After the first few preliminary trials had given promise of a decided result, a micrometer screw was added, instead of the support at M, in order to be able to form an approximate idea of the distance between the plates during an experiment.

The copper and zinc plates of the condenser were first carefully faced up to a plane surface by the use of a surface plate, and then lightly ground together with washed emery-powder, after which the zinc received a light rubbing with fine emery-paper. Wire connexions were fixed by screws to each plate, and the pair could thus be joined by means of a mercury cup arrangement either to a reflecting galvanometer, giving a deflection of about seventeen divisions for a millionth

* [When the quadrants of copper and iron were disconnected and then joined by a drop of potassium sulphide solution, the difference of potential near them was (as would be expected) increased instead of annulled. It became about double its former value.—November 1, 1886.]

ampère current, or to a circuit consisting of a Leclanché cell and an ordinary astatic galvanoscope. A telephone was also generally included in the circuits. When joined up with the cell in circuit it was possible by very careful adjustment of the distance between the plates to find a point where although they were not in metallic contact still a current would pass. The needles of the galvanoscope (which flew to the stops when the plates were in actual contact) were deflected unsteadily to about the same extent as if the condenser were replaced by a resistance of 50 to 100 ohms, and a faint hissing sound was heard in the telephone. If now the terminals from the plates were transferred to the galvanometer, a current was observed varying in different experiments according to circumstances from a few up to 130 divisions, but which at once ceased when the plates were either placed in metallic contact or so far apart as to separate the films on them.

31. Measurements of the thickness of the two films were made by the micrometer screw at M. Its indications are, however, only approximate, since the upper plate does not remain parallel to the lower while being raised; and also (the whole apparatus not being very rigid) it is quite possible that when the upper film rested on the lower one, there was sufficient pressure on the surface of the plates to prevent the upper one falling to the extent indicated by the micrometer readings, although a weight of six pounds was placed on the end of the upper board at A to help to depress it. I give, however, a series of readings typical of those obtained in all the experiments.

M denotes the reading on micrometer corresponding to the distance through which it rose in thousandths of an inch. D is the deflection on galvanometer. (The adjustment for great sensitiveness rendered its zero unstable.)

Hygrometric state of air measured by Regnault's form of hygrometer was 0·77.

M=	0·5	0·7	1	1·5	2	2·5	3	3·5	4	4·5	4
D=	10	90	70	90	70	55	40	40	25	10	10

Plates in contact.　　　　　　　　　　　　　　　　　Films apart.

M=	3·5	3	2·5	2	1·5	1	0·5	0
D=	35	38	40	50	50	50	15	5

Plates in contact.

Hygrometric state of air = 0·655—

M=	0	1	1·5	2	2·5	3	3·5	3	2·5	2	1·5
D=	30	65	68	75	65	40	32	32	58	67	35

Plates in contact.　　　　　　　　　　　Films apart.

The plates were very carefully dusted before use with a camel-hair brush, and it was necessary also to avoid breathing on them, as

the slightest puff of breath over them caused the formation of a film,
which, though quite invisible, easily formed enough current to send
the index quite off the scale.

32. I now made some experiments to ascertain whether the film cell
could be polarised by the current from a Leclanché element connected
to the plates.

The following examples show that this is so, and that the polarisa-
tion effect is so great as at first even to overpower the ordinary
electromotive force of the film cell.

Column I gives the mode of connexion of the poles of the cell to
the plates ; P the carbon pole.

II.—The deflection observed on the galvanoscope.

III.—The zero point of scale of reflecting galvanometer.

IV.—Its initial swing on having the terminals of film cell changed
to it.

V.—The point at which the index rested after its first swing.

(1.) Hygrometric state of air = 0·8—

I	II	III	IV	V	
P to Cu......	25	17	..	30	Falling.
P to Zn......	71	20	..	16	Rising.
			Readjusted plates.		
P to Cu......	12	30	..	45	Falling.
P to Zn......	68	32	..	22	Rising beyond 32.
			Readjusted plates.		
P to Cu......	16	40	60	47	Falling.
P to Zn......	74	44	31	40	Rising.

(2.) Hygrometric state of air = 0·826—

I.	II.	III.	IV.	V.	
P to Cu......	52	12	60	30	Falling.
P to Zn......	74	21	14	..	Rising till after some minutes the deflection passed the zero, showing the ordinary current from film cell.

[32a. Several of the foregoing experiments go to show that a cessa-
tion of chemical action at the surface of the plates implies a subse-

quent disappearance of the difference of potential near them, and a decrease of the former produces a subsequent decrease of the latter.

In the case where the decrease of chemical action is due to drying, it is, perhaps, sufficiently in correspondence with the theory to suppose that when the film is partially removed, the effect it produces should also partially disappear, although we may not be in a position to specify the particular nature of the molecular process involved, or whether there is included with it anything of the kind described next following.

In the case, however, of the hindrance of chemical action by the formation of an intervening oxide or other compound layer, there appears at first sight a difficulty, since it may be said that after the separation and disposal of the two opposite charges on the two films resident on the metals in contact as above described, the mere formation of intervening oxide on other layers would tend more to keep these charges apart than to allow them to combine.

It must, however, be remembered that in this case the films themselves are also in contact, and that a conducting connexion between them may reasonably be supposed to provide a continuous leak, by which the difference of potential suffers a constant reduction below the normal, and would, therefore, disappear altogether, if the leak were not greatly overpowered by continuous electrolytic combination at the surface of the metal.

The lateral resistance of the film must of course be very great, in order that so much difference of potential may be observable ; but it is obvious that unless the film were of infinite conductivity some difference would still exist.

Where the metals are not in immediate contact the films on (or moisture in the pores of) the supports may readily provide the necessary electrolytic connexion, considering the very small quantities of electricity involved. I have observed that when the vulcanite piece, M, fig. 1, carrying the quadrants, became damp from remaining some days inclosed with the water in the vessel below it, the potential difference was considerably decreased.

The existence of "local action" or local currents in the film would seem also not improbable, and would account for some of the phenomena connected with tarnishing, otherwise difficult to explain.—November 1, 1886.]

33. I may here refer to an experiment made prior to these last but related to them. It was based on the supposition that the molecules of water in the condensed film on a metal must (in order to oxidise it) have their oxygen atoms turned and attracted towards it, but if we could reverse this arrangement by attracting the hydrogen atoms, we might be able to retard the oxidising action. Possibly the fact that the potential for a charged conductor is constant throughout

negatives this view. It was thought, however, the results might throw light on questions as to the molecular nature of any electro-chemical polarisation of the condensed films as a cause of the static voltaic effect, and for that reason they are here shortly stated. The condenser, fig. 3, was provided with a pair of zinc plates faced up together. The difference of potential of their films after metallic contact of the plates was tested qualitatively by a quadrant electro-meter in the usual way. A very small value was found, due doubtless to some slight difference in the state of their surfaces. The plates were then separated to a small distance, and joined to the opposite poles of a battery of 100 Daniell cells. After $17\frac{1}{2}$ days the battery was removed, and the difference of potential of the films on the plates again tested. It was supposed that if any greater oxidation of the positively electrified plate, as compared with the other, was caused by polarisation of the films, there would be a greater difference of potential than before ; the film on the tarnished plate being negative. If anything, the reverse was the case, but the effect was very slight, and may have been due to some kind of storage cell action in the supports of the plates. A second trial with the Daniell battery joined the reverse way gave a like negative result. Probably the effect suggested does not take place, or it is masked by local actions in the film.

34. An old experiment of Gassiot ('Phil. Mag.,' vol. 25, 1844, p. 283), where electrical disturbance is produced by altering the capacity of a Volta condenser without contact between its copper and zinc plates, which are merely connected to the gold disks of an electroscope, is assumed by some authors (Von Zahn, 'Untersuchungen über Contactelectricität,' p. 55 ; Wiedemann, 'Lehre von der Elektri-cität,' vol. 2, p. 988) to be difficult or incapable of explanation by the contact theory, though I think wrongly so, as there is contact of dissimilar metals, viz., copper-gold and zinc-gold on the connexions to the gold disks of the electroscope used. (Von Zahn's inability to repeat the experiment so as to get Gassiot's result seems to me unaccountable.)

35. In order to exclude any uncompensated contact of dissimilar metals, as in Gassiot's experiment, I modified it by joining the copper plate of the condenser, fig. 3, to the copper quadrant in the electro-meter, fig. 1, and the zinc plate to the zinc quadrant. The latter connexion was made by a copper wire, but the dissimilar contacts thereby introduced compensate one another.

On altering the capacity of the condenser a very decided alteration of the potentials near the quadrants was observed. The following table gives the results :—Column I gives the sign of the electrification of the needle. II, the position of the index with condenser plates apart. III, the point to which the index swings on closing them to

within about 0·01 inch.   IV, the point where index came to rest
with the plates so closed.   V, the swing on separating the plates.
VI, the final deflection with plates apart.   The prefix L signifies a
left-hand deflection towards the copper quadrant; R a right-hand
one towards the zinc quadrant.

I.	II.	III.	IV.	V.	VI.
+	L 44	L 29	L 38·5	L 55	L 43·5
−	R 55	R 39·5	R 48·5	R 66	R 54
−	R 54	R 38	R 48	R 63·5	R 53·5
+	L 44	L 33	L 39	L 51·5	L 43·5

It is evident there were electrical charges present, although there
was no actual metallic contact at which any " Scheidungskraft "
could exist to produce them.   (See Appendix.)

36. In conclusion, the following diagrams represent the distribution
of potential according to the theory here adopted.

Fig. 5 gives the state of things in a closed zinc-water-copper cell of
uniform resistance throughout its circuit; N and P understood as
joined in closed circuit.

Fig. 6 shows the same cell with the metals apart ; the two metals
being covered with moisture films, which are practically a portion of
the electrolyte and (in so far) at the same potential.   This shows
also graphically the explanation of Sir William Thomson's " water-
drop " experiment, referred to before (§ 28).

Fig. 7 is a cell divided in the copper part of the circuit, where
instead of the potential of a film on the zinc, as in fig. 6, we have the
lower potential of that on the copper piece connected to the zinc.
The terminals of like metal in this way permit the electromotive
force of the cell itself to be measured in the usual electrometric way.

Fig. 8 represents either a zinc-water-copper cell divided in its
electrolyte, or the ordinary static experiment where the difference of
potential of the films on two metals in contact is measured.

It is to be borne in mind that these diagrams are only of a qualita-
tive nature, as the difference of potential between the dry metals and
water, &c., in contact with them has not yet been experimentally
determined.

Appendix.

The experiment described, § 35, leads to the following theoretical
considerations which have been in part suggested and put into form
by Mr. J. Larmor, of St. John's College, Cambridge.

37. The zinc sector of the electrometer and the zinc plate of the condenser in connexion with it form an insulated conductor of zinc; the copper sector and the copper plate of the condenser form an insulated conductor of copper. Consider first the hypothesis which asserts that after recent metallic connexion, the potential of the zinc exceeds that of the copper by a definite amount. The plates being primarily at a distance, make them approach each other gradually. As they do so the experiment shows that the difference of potential between them gradually diminishes. Their behaviour is just that of an ordinary charged condenser; as the plates come closer together their capacity is increased, being always inversely proportional to their distance, and therefore for a given charge the difference of potentials is diminished, being always directly proportional to their distance. By bringing the plates very close together their difference of potential may be reduced indefinitely. Having brought them within a very minute distance of each other, establish metallic connexion between them. According to the hypothesis this restores them to their original difference of potential. This is done by the separation of a quantity of electricity equal to the difference of potential multiplied by the capacity of the condenser; the two plates acquire charges of this amount but of opposite signs. This operation involves a gain of energy to the system of amount equal to half the capacity of the condenser multiplied by the square of the difference of potentials. The plates being very close together these quantities are of considerable magnitude. Now the operation of making metallic contact was merely directive and involved no supply of energy from without. This supply must therefore come from an absorption of the heat of the system, or from chemical combination either partial or complete. The first alternative is inadmissible, as it would lead to a perpetual motion; we are, therefore, driven to that of chemical combination, which may either be an action between the zinc and copper at the point where the metallic connexion is made, or an action between one or both of the metals and the surrounding gaseous medium. In either case its amount, though very minute, is not infinitesimal. As there is no evidence of any action between clean zinc and clean copper at ordinary temperatures which involves any liberation of energy worth considering, it seems nearly certain that the actual liberation of energy is due to the other cause, which in the atmosphere is oxidation whether nascent or complete.

The plates with their acquired charges may now be separated by mechanical energy, and their charges imparted to an electric receiver by contact. The plates being now as at first the same cycle may be repeated indefinitely, and a permanent supply of electricity may be thus theoretically obtained at the expense of continued oxidation of the plates in air.

These considerations apply very much in fact to Sir W. Thomson's gravity battery with copper filings and zinc funnel.

38. But now suppose that any atmosphere capable of acting chemically on the plates has been removed. On bringing them close together and making metallic connexion between them, they will not be able to return to their original difference of potential, for the energy required to effect the electrical charge is no longer forthcoming. The facts thus far encourage us therefore to hold the view that the difference of potentials is not an intrinsic property of zinc and copper in themselves, but is the result and manifestation of the fact that their contact in the atmosphere has started a chemical action which has proceeded till choked off by its own results.

According to the ideas of the theory of chemical equilibrium of Clausius, Gibbs, and Helmholtz, it has proceeded until the accumulation of its products has secured that further progress shall not any longer lead to a dissipation of energy.

39. If this argument which refers the difference of potential to an initial chemical action on the surface of the plates where they are in contact with the atmosphere or to a condensed liquid surface film derived from it, be allowed, the next step would be the assignment of some mode of action which would account for the result. And here the idea of a double electrical layer, which has been elaborated by Helmholtz from the phenomena of electrolysis, and so successfully applied by him in explanation of the polarisation of voltaic cells, comes up hopefully.

The oxygen of the moisture in the atmosphere will under proper circumstances combine chemically with the zinc, giving rise to electrical effects, as in Sir W. Thomson's gravity battery already mentioned. When the circumstances are such that actual combination is not possible, the two substances will feel each other's presence, and take up along their surface of contact a conformation of molecular equilibrium; we have a right to assume that this configuration will present a sheet of positively charged atoms, facing an equal sheet of negatively charged atoms, and thus forming a double layer. A precise explanation of how this comes about could hardly be required of us, for so long as we continue to apply to such questions our ordinary notions of electrical attractions at all, there is no way open for explaining the dynamical fact of a difference of potential between two substances in contact, except the assumption of such a layer along the surface of contact. How it is formed may be at any rate illustrated from the phenomena of voltaic polarisation.

40. We may then provisionally contemplate a zinc plate as surrounded by such a double layer, negative inside and positive outside; and a copper plate as surrounded by a similar layer of smaller moment, the moment being measured in the same way as for magnetic
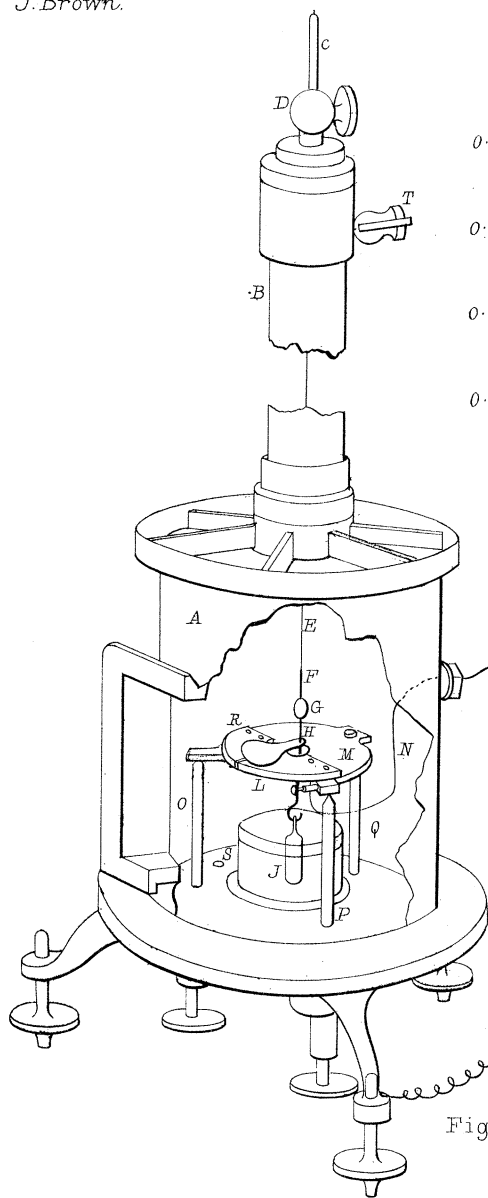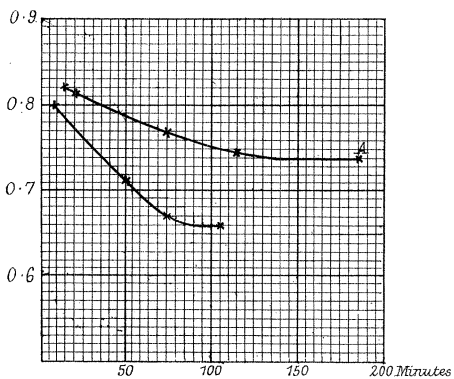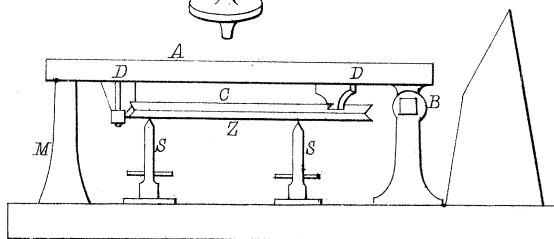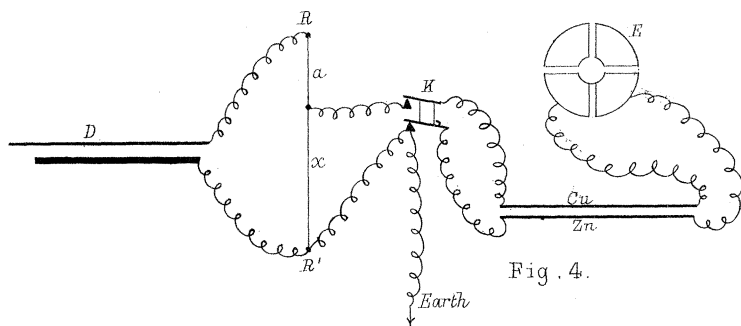
Fig. 2.

Fig. 1.

Fig. 3.

R

E

a

K

D

x

Cu

Zn

R'

Fig. 4.

Earth

H₂O

N

Cu

P

Zn

Fig. 5.

Film on Zinc

Film on Copper

H₂O

Cu

Zn

Fig. 6.

Film on Copper

Film on Copper

H₂O

Cu

Cu

Zn

Fig. 7.

Film or Water
on Zinc

Film or Water
on Copper

Zn

Cu
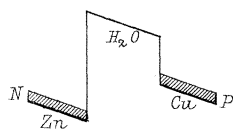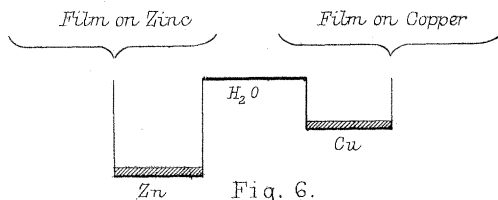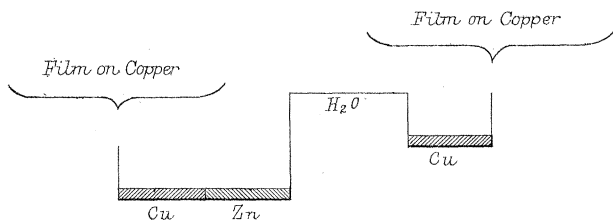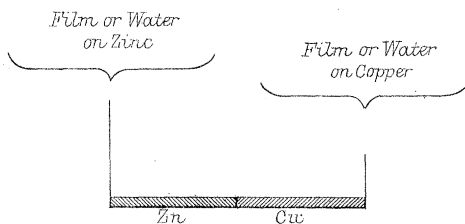
Fig. 8.

shells, by surface density multiplied by distance between the com-
ponent layers. When the two plates have attained electrical equili-
brium with surrounding objects, the potentials just outside the layers
will be equal (*e.g.*, by electrolytic connexion as in Sir W. Thomson's
experiment of a zinc and a copper plate connected by a drop of water),
but the potentials of the metals inside will be different, each being
less by the moment of its layer. The zinc will therefore be at a
lower potential than the copper. If a metallic connexion is now
made between the metals, positive electricity will flow from the
copper to the zinc until the potentials of the metals are equalised,
and the difference of potentials of the air outside the plates will now
be exactly opposite to that which subsisted between the metals before
metallic contact.

There is this difference between the view just mentioned and that
of pure contact difference which was examined, § 37, that here the
metallic connexion involves a running down of electric energy, while
there it involved an addition of energy from without.

41. The explanation by superficial double layers once accepted,
there is no longer any reason for retaining contact of the two metals
as one of the conditions necessary for the setting up of this action
between a metal and its surrounding atmosphere.

We may hold that when a piece of clean zinc, or a piece of clean
copper, kept insulated, is introduced into an atmosphere capable under
favourable circumstances of acting chemically upon it, a change of a
chemical or semi-chemical character is thereby initiated over its
surface, which involves a transformation of energy, though in minute
quantity, and which proceeds until a state of equilibrium is estab-
lished, as indicated by the setting up of a certain definite difference
of electrical potential between the metal and the gas near it, but out-
side the sphere of the action.

VI. " The Coefficient of Viscosity of Air. Appendix." By
HERBERT TOMLINSON, B.A. Communicated by Professor
G. G. STOKES, P.R.S. Received November 15, 1886.

(Abstract.)

In the previous experiments by the author on this subject the
coefficient of viscosity of air was determined from observations of the
logarithmic decrement of amplitude of a torsionally vibrating wire,
the lower extremity of which was soldered to the centre of a hori-
zontal bar. From the bar were suspended vertically and at equal
distances from the wire a pair of cylinders, or a pair of spheres. The
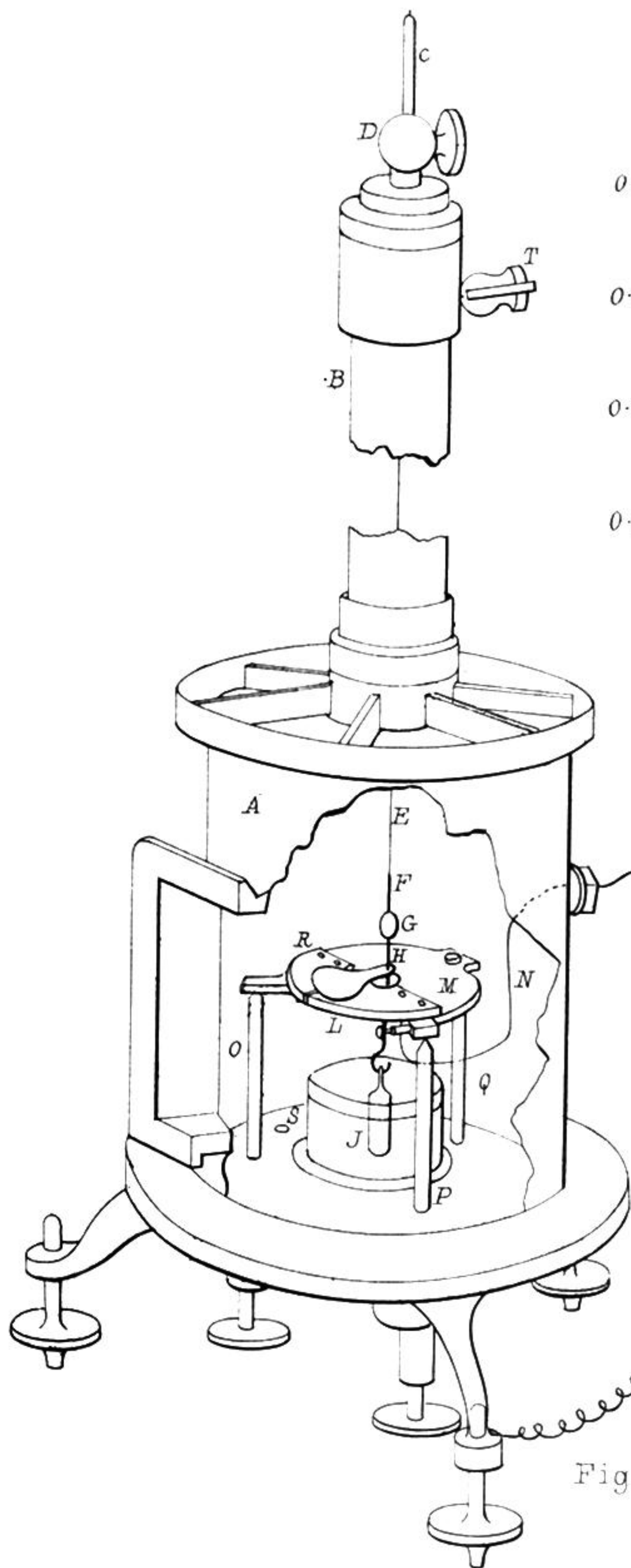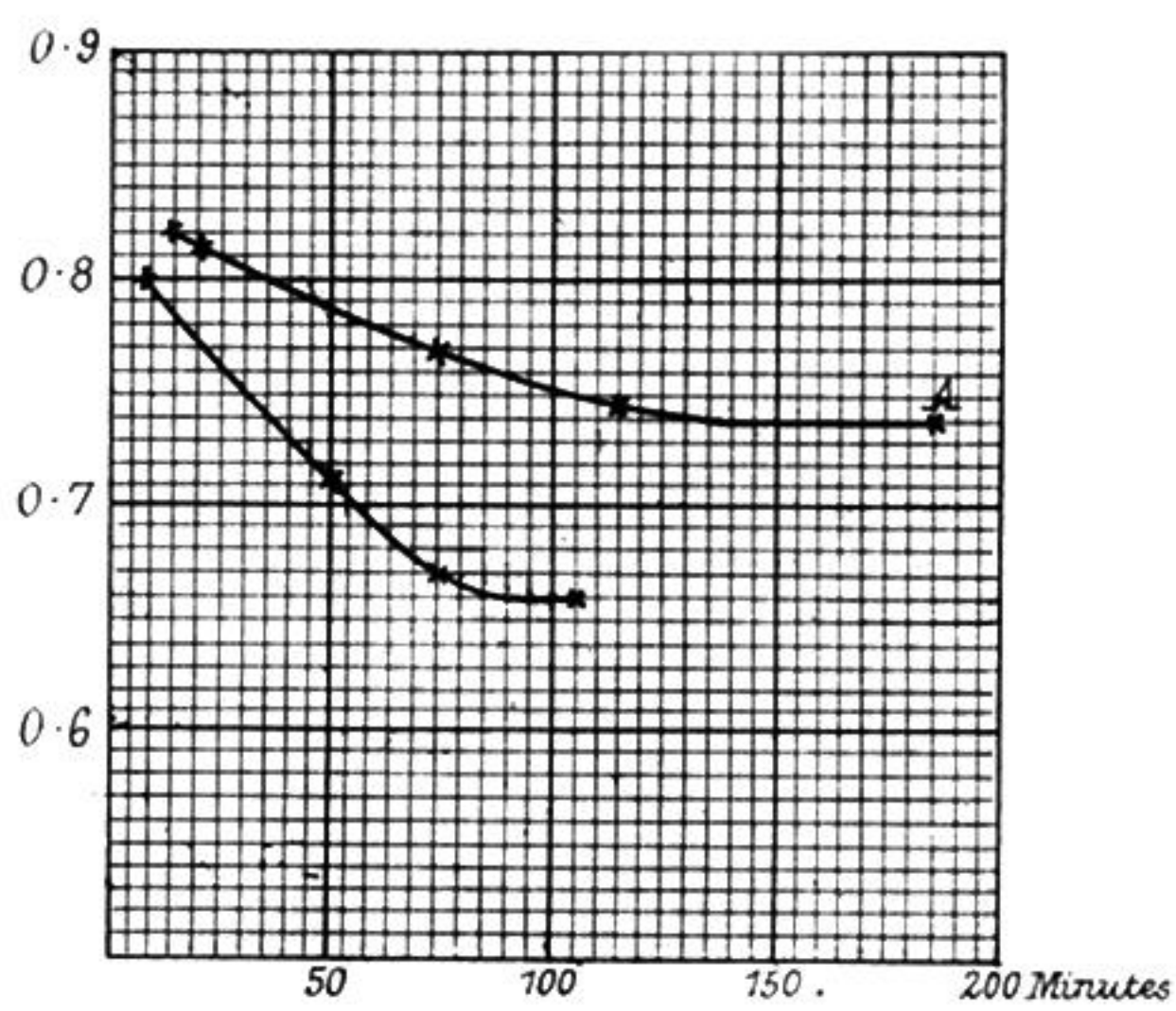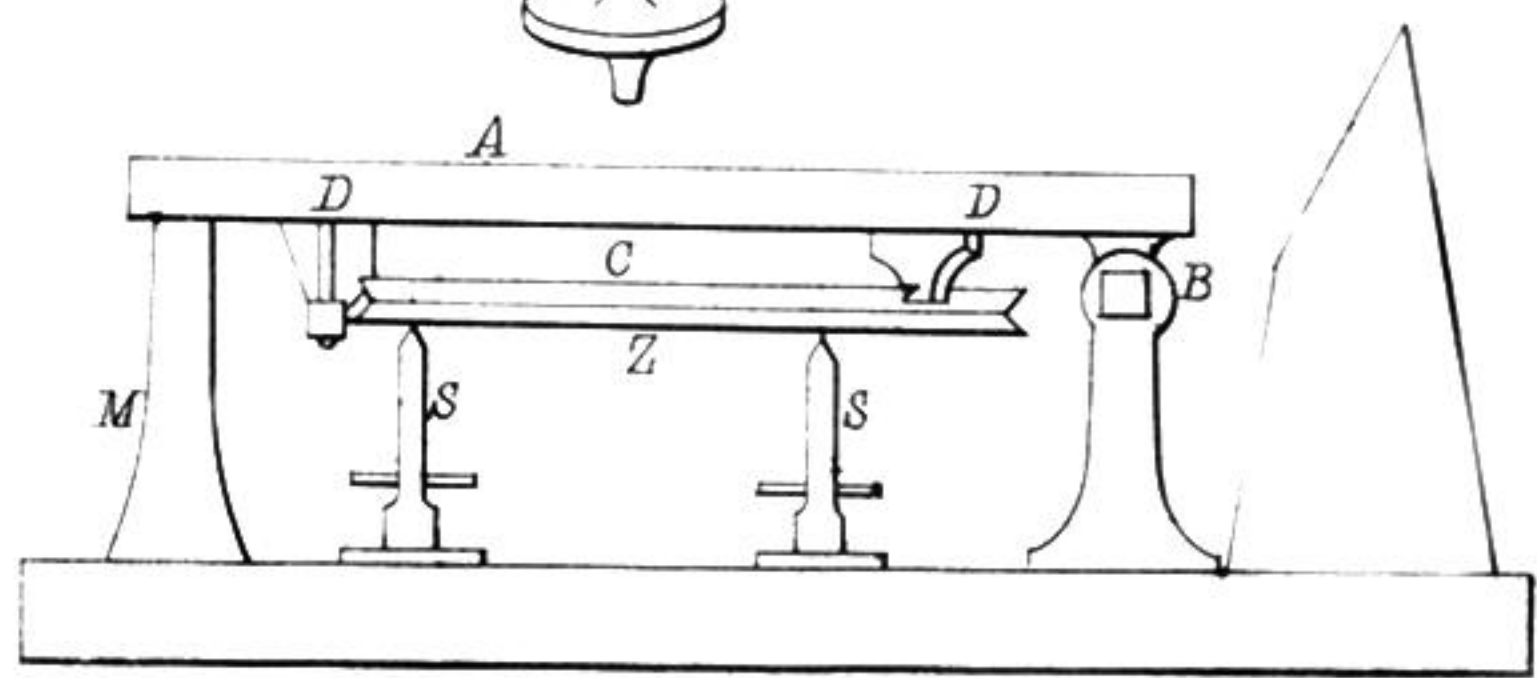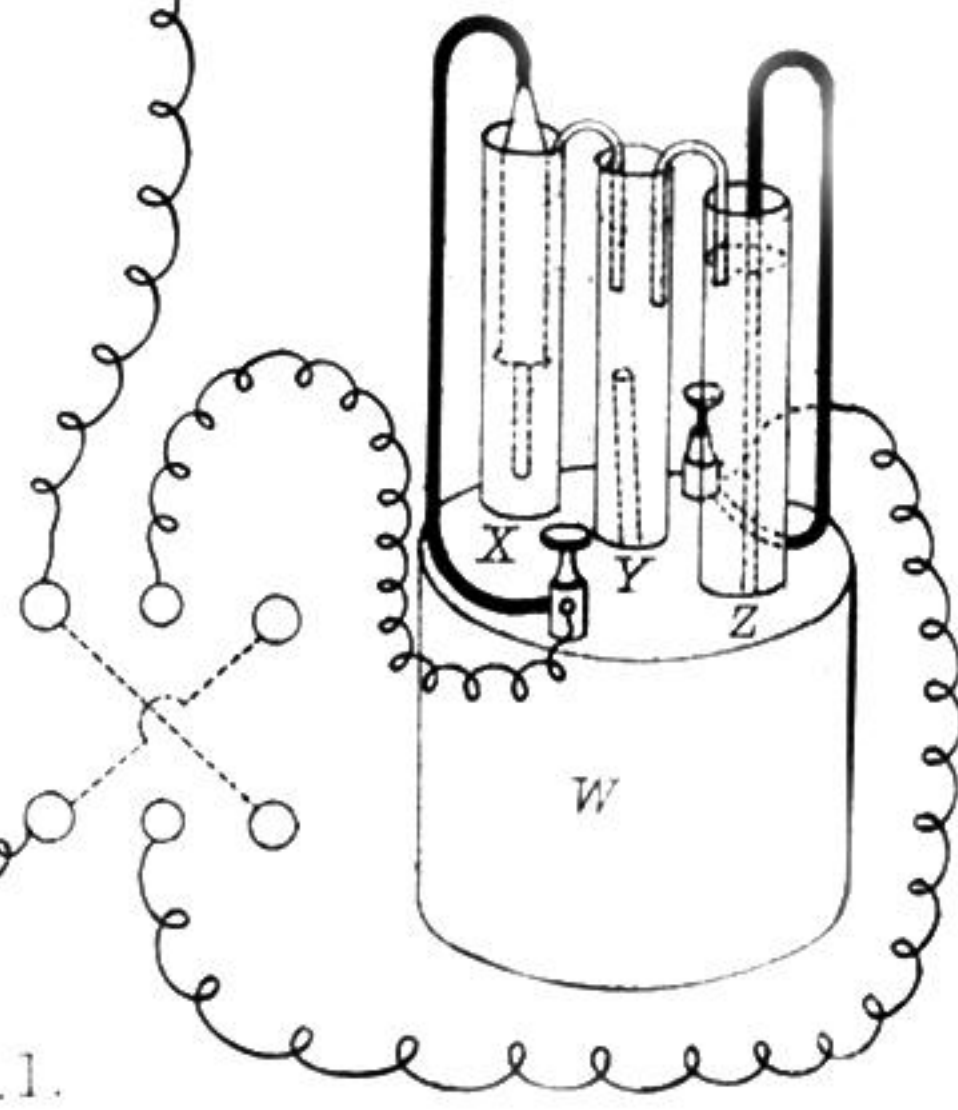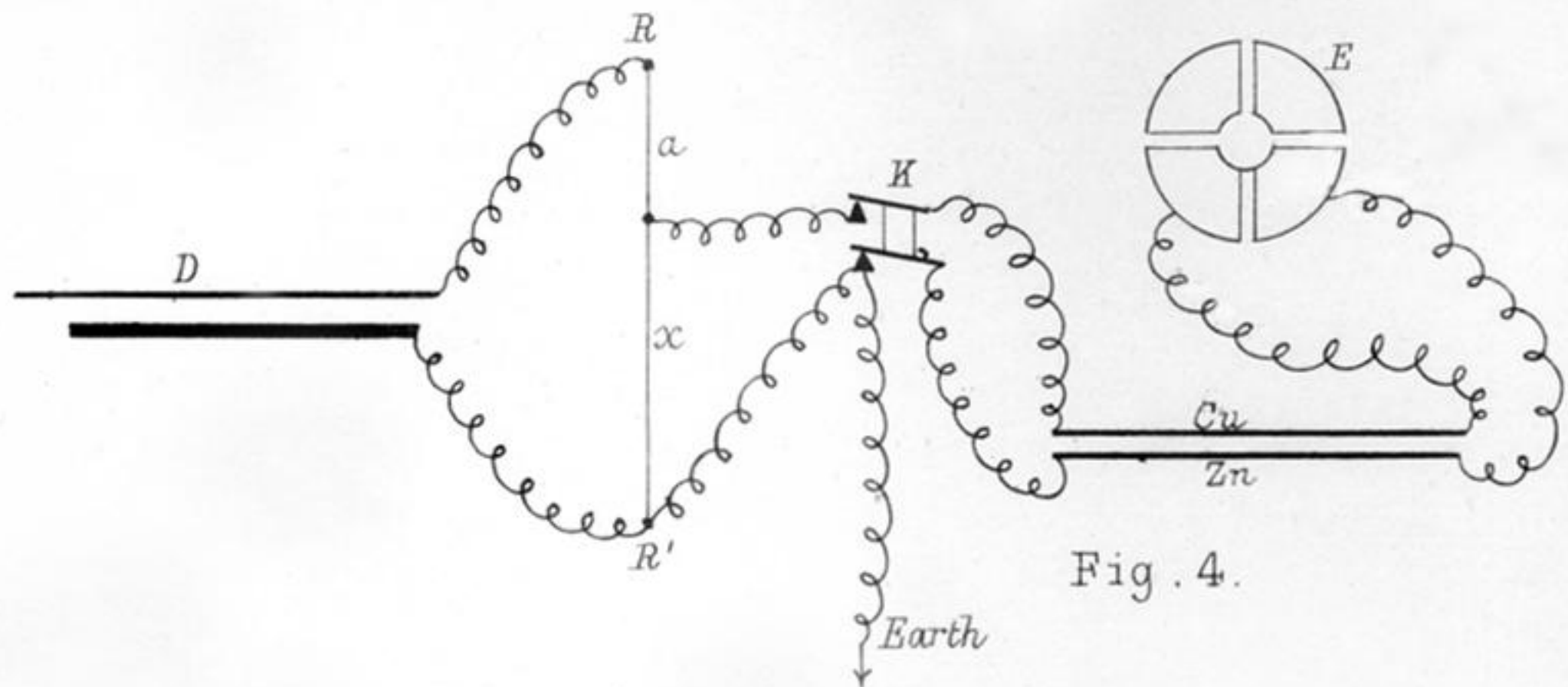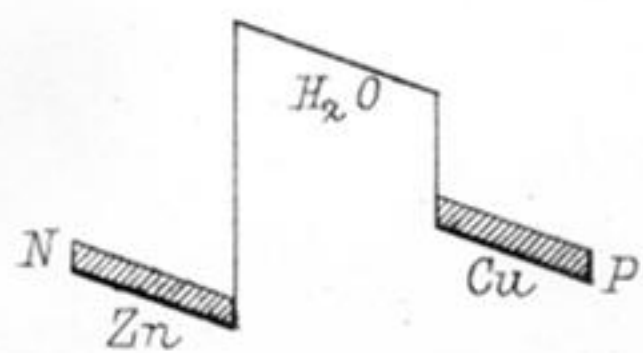distances of the cylinders or spheres from the wire were such that the

Fig. 2.

Fig..1.

Fig. 3.

Fig. 4.

Fig. 5.

Fig. 6.

Fig. 7.

Fig. 8.